



The effect of tape casting operational parameters on the quality of adjacently graded ceramic film

Bulatova, Regina; Gudik-Sørensen, Mads; Della Negra, Michela; Andersen, Kjeld Bøhm; Kaiser, Andreas; Bahl, C.R.H.

Published in:
Ceramics International

Link to article, DOI:
[10.1016/j.ceramint.2015.11.042](https://doi.org/10.1016/j.ceramint.2015.11.042)

Publication date:
2016

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Bulatova, R., Gudik-Sørensen, M., Della Negra, M., Andersen, K. B., Kaiser, A., & Bahl, C. R. H. (2016). The effect of tape casting operational parameters on the quality of adjacently graded ceramic film. *Ceramics International*, 42(4), 4663-4671. <https://doi.org/10.1016/j.ceramint.2015.11.042>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

The effect of tape caster operational parameters on the quality of adjacently ceramic film

R. Bulatova, M. Gudik-Sørensen, A. Kaiser, M. D. Negra, K. B. Andersen, C. R. H. Bahl

Department of Energy Conversion and Storage, Technical University of Denmark – DTU,
Frederiksborgvej 399, DK-4000 Roskilde, Denmark

Abstract

The optimum condition among tape casting with single blade, double blade, using pump system and a proposed continuous speed change mode has been analysed for the purpose of forming green tapes of constant thickness. Advantages and limitations of every method are described here. The tape casting experiments were conducted using a solvent-based slurry and were built to be as generic as possible in order to allow the control of various processing conditions.

The single-blade tape casting technique from this study has been used for side-by-side tape casting of strontium doped lanthanum manganite oxide $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM) slurry next to slurry, consisting of a mixture of LSM and gadolinium doped cerium oxide $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (CGO). In this work the influence of the geometric parameters of the partition, dividing the casting tank into chambers, on the quality of graded tape were studied. It was elucidated that at casting speeds above 30 cm/min and the shortest partition ‘tongue’ beneath the blade favours the formation of smooth graded tapes, while lower casting speeds and the presence of a partition tongue results in splitting and formation of a gap in the confluence area.

Introduction

Needs in manufacturing a functionally graded film grows together with development of such advanced technologies as solid-oxide fuel cells, piezoelectric devices, batteries, capacitors and actuators production. Tape casting (film casting, doctor blading, doctor blade casting), initially invented for manufacturing ceramic capacitors with the aim to improve dielectric properties and densify a microelectronics package [1], now is widely implemented into other advanced technologies. A wide range of shaping solid loads such as ceramic, polymeric, glass or metal particles of nano- and micro-sizes into thin, uniformly flat, hard or flexible films of tens meters, if required, is the one side of tape casting development. Nevertheless, in order to surpass more a machinery modern forming techniques and still tailor the requirements of smart technologies, the design of tape caster tank itself often has to be modernized. For instance, modernization of casting head included the inclination of the back wall of the tank, aiming to uniform the fluid flow inside the reservoir [2].

In the scope of enhancement the efficiency of advanced functional graded materials, the new side-by-side tape casting (SBS TC) (adjacent co-casting) forming technique has been invented. The fact that co-casting method itself was independently proposed by two scientific groups, working on magnetic refrigeration [3] and on improvement of a laser gain element [4], shows the high potential of SBS TC for gaining a broad commercial acceptance and development. Having the general idea of co-casting in common, these two works differed both by recipe composition and processing parameters. Kupp *et.al.* [5] tape cast xylenes- and ethanol-based slurry loaded with particles of micro- and nano-sizes; tapes were fabricated with a casting gap of 0.356 μm and a casting speed of about 70 cm/min. For magnetic cooling thicker films were required [6], so the graded tapes of micro-sized ceramic particles

were fabricated from the methylethylketone-based slurry using a gap of a 1000 μm and a casting speed of 20 cm/min. As it is seen, SBS cast tapes are possible to shape in a wide range of casting speeds and gaps with dissolving powders of both nano and micro sizes in organic solvents. Optical properties of Er:YAG graded tapes and magnetic properties of LCSM graded tapes were proven to be comparable with performances of typical commercially applied materials. Another critical difference in given works was the design of partition (divider). In Kupp's et.al. work [5], divider was made of steel and covered the whole tape caster reservoir and the gap under the shearing blade. Authors of magnetic cooling work used a Teflon partition, 1.95 mm wide and covering just the reservoir space, co-flowed slurries were sheared together underneath the blade.

Another aspect of dividing casting tank into segments is the target to improve alignment of elongated particles into the casting direction, since a torque, generated next to the tank walls, was proven to affect the particles rotation even more than a basic concept of increase in casting speed [5, 6]. In comparison of a set of tapered blades installed 5 mm apart from each other at the exit of the tank and array of sharpened pins 0.7 mm from each other, the latter ones shown to exhibit a higher degree of particles orientation in cast tape [8].

As one can see, the new idea of separating a standard casting tank into compartments came as an engineering solution for solving as different tasks as joining dissimilar materials into functional graded tape and forming of high-ordered thin films, however, optimization and study how partitions geometrical parameters affect the quality of cast tape is still missing. Current work is aimed to define and explore systematically which features of tapes is possible to control changing the design of the partition and changing the casting speed as one of the setting of machinery characteristics. For that, slurry with a solid load of ceramics strontium doped lanthanum manganite oxide $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM) and another slurry, consisting a mixture of LSM and gadolinium doped cerium oxide $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (CGO) were co-cast.

In all three works [1, 2, 6], described above, tapes were cast using a single-blade system. However, nowadays lab-scale doctor blading technique use a double-blade system aiming to diminish the effect of the hydraulic pressure (pressure-driven flow, *Poiseuille flow*) on the tape thickness formation. The effect of hydraulic pressure stems from the differences in slurry level on opposite sides of the casting blade, affecting the actual slurry speed (shear-driven flow, during tape casting [9]). This pushing the slurry out of reservoir by a hydraulic force in addition to pulling force applied by a moving carrier (shear-driven flow, drag-driven flow, *Couette flow*) increase the total volume flow below the casting gap results in welling of the slurry right after it pass the blade. In some cases, due to welling the wet thickness of the tape exceeds the casting gap height.

Hence, the review of methods available in tape casting is proposed here in order to distinguish, first, which tape caster design guarantee a stable uniform slurry flow for the whole shaping process; and afterwards study the influence of the partition shape using selected tape caster design. Among tested, the double-blade system is the lab-scale solution for stabilizing the fluid flow and minimizing the effect of the hydraulic pressure drop behind the casting blade. Industrial finding differs mainly because of the higher volume of slurry used, which is supplied continuously on the long moving belt by a pump system. Another novel method of keeping tape thickness constant was invented as analysis of results of our previous work [10]. The concept relies on two simultaneous processes: at the beginning of the process the tape is usually thicker because of the cumulative effect of shear-driven viscous drag due to the peeling move of the substrate and pressure-driven hydraulic pressure

generated by a slurry column in reservoir; the second approach implies tape thinning with increase in casting speed [10], [11]. Therefore, the forth of proposed method is based on compensating the hydrostatic pressure decrease by a gradual decrease in casting speed.

Current study is comprehensively divided into two parts: establishing the tape caster design and a casting program with a focus to achieve a stable flow and uniform tape thickness, in another words, aiming to minimize or eliminate the hydrostatic pressure drop during the experiment. The second part of this study is devoted to clarification how partition design affects the graded tape formation at various casting speeds. As the output parameters for both adjacently cast slurries the tape thickness consistency and the interface shape between materials were controlled.

Experimental procedure

1. Raw materials and slurry preparation

The SBS cast tapes were prepared by adjacent co-shearing of two slurries. The first slurry contained 14.25 vol% of $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ (LSM, Haldor Topsoe A/S, Denmark; calcined at 1200°C for 2 hours, arriving at a specific surface area of 18.0 m²/g). The second slurry had 9.59 vol% LSM and 0.90 vol% of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$ (CGO, Rhodia, France; uncalcined, specific surface area of 12 m²/g) as solid loading. The choice of powders used is based on the wide usage of these ceramics in various applications [12], [13] with tape casting as the shaping technique. Another reason for using LSM and CGO is the difference in particle morphology and color, which facilitates detection of the interface between co-cast materials both visually by color and electronic microscopy due to the powders morphological and chemical differences.

Slurries were prepared according to the standard MEKET (azeotropic mixture of methylethylketone and ethanol) based recipe [9], [11], [14]. Uniform distribution of chemicals and fine grinding of particles in highly viscous slurry was achieved by the division of the milling process into steps. The detailed description of slurry content and workflow are given in our previous work [11].

In order to be able to compare and reproduce results from different tests, each step of slurry preparation has to be precisely controlled. To attain that, particles size distribution was measured during the whole period of the slurry preparation using Scattering Particle Size measurements (Beckman Coulter LS 13320, Miami, FL).

2. Rheological characterization

The apparent viscosity (η) measurements were conducted with pre-shearing and reversing increase of shear rate up to 50 s⁻¹ using a cone-plate system (angle 1°) at 21 °C (MCR 301, Anton Paar GmbH, Graz, Austria), as shown in Figure 1. A solvent trap was used to minimize the evaporation of organic solvent during the rheological measurements. Both LSM and LSM_CGO slurries were characterize with a shear thinning behavior as required for tape casting.

Flow curve test (inset in Figure 1) showed that both LSM and LSM_CGO slurries possess an extremely low yield stresses, therefore the flow behavior of the slurries can be described by the Ostwald-de Waele power law fluid behavior:

$$\tau = k\dot{\gamma}^n \quad (1)$$

where τ is the shear stress, $\dot{\gamma}$ the shear strain rate, k the constant describing the consistency of fluid, and n the constant describing deviation from the Newtonian flow. Due to thixotropy, viscosity curves for both LSM and LSM_CGO slurries yield individual hysteresis loops. The rheological behaviour and power law constitutive equation fit were chosen to be described by the reverse viscosity curves as they characterize the re-built viscosity. Fitting the experimental data of Figure 1 to Eq. 1, relatively high values of the correlation coefficient were obtained (Table 1), demonstrating a good compatibility of slurry fluid behavior with the Ostwald-de Waele power law model.

Table 1. Ostwald-de Waele power law model's fitting parameters and correlation coefficient.

	k	n	R ²
LSM	6.63(2)	0.73(3)	0.994
LSM_CGO	6.19(2)	0.77(3)	0.996

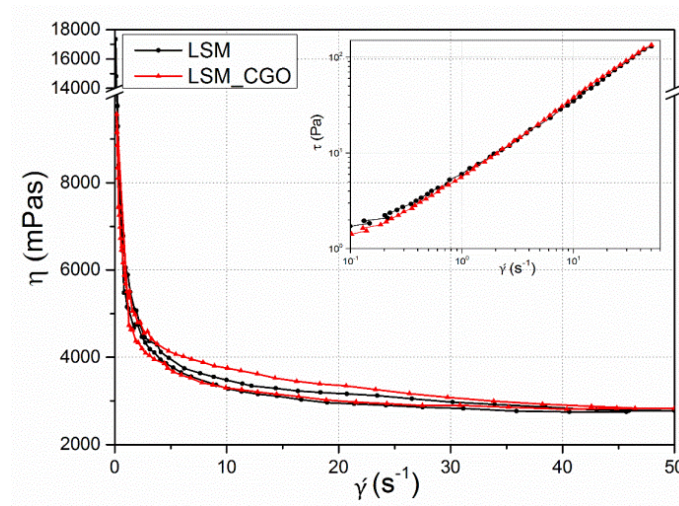


Figure 1. Viscosity and flow curves of LSM and LSM_CGO slurries.

In order to study how the rheological behavior of the slurries changes during the entire process of tape casting, the casting process was reproduced on the rheometer, using a specially built four step program (see Results and Discussion). To imitate the slurry drying process during the tape casting process, a spindle with 6 holes on its surface was implied. The test was performed using the spindle of 25 mm diameter with holes on top in order to improvise the drying process allowing the solvent to evaporate through these holes.

Before tape casting, LSM and LSM_CGO slurries were filtered through a 100 μm meshed tulle with a further de-airing step in a vacuum pump (100mBar) in order to remove air bubbles from the slurry volume. Slurries with viscosities (η) of about 4000 mPas at 3.3 s^{-1} shear rate ($\dot{\gamma}$) for both LSM and LSM_CGO were used for tape casting as discussed in Ref. [11].

3. Tape casting

3.1. Tape casting in the thickness control experiments.

LSM and LSM_CGO slurries were tape cast adjacently using a Teflon partition of 1.95 mm width, completely separating the two slurries into 4 cm wide sub-reservoirs [11]. The blade gap height was kept constant at 1 mm, and the casting speed for all experiments was 30 cm/min, except the fourth experiment, where the casting speed was changing. The

partition with no division (no partition 'tongue') underneath the casting blade was used for all tests. At the beginning of every test the casting gap was closed by Duct tape to ensure the simultaneous flow of adjacently cast slurries. Four different techniques for adjacently casting slurries were tested as described below.

Single-blade tape casting (SB) was taken as a reference test. The precise description of the casting head setup is described in details by the authors earlier [11], [15].

Double-blade tape casting (DB) is used in laboratories as a solution for avoiding a continuous slurry level decrease in the casting head. According to the work of Zhang's et al. [16] on precise thickness control in tape casting, the rear gap was chosen to be at 1.2 mm height, and the front casting gap was fixed at 1 mm height. The partition had a more complicated shape, since it had to separate the tank both in the slurry loading reservoir, beneath the backside blade, and in a narrow supplemental reservoir between two blades. Besides, all joints between partition and caster walls, partition and blades had to be isolated with Duct tape in order to prevent leaking of slurries from adjacent sub-reservoirs. This introduced some non-controlled inaccuracies into the DB setup.

With the requirement to tape cast continuously for a long time with a steady slurry stream, industry normally employs a pump system in tape casting (PS). This method benefits in keeping the slurry under pressure and continuously agitated ensuring homogeneity of the slurry; besides, the slurry column in the reservoir in this case is constant during the whole process providing a uniform wet tape thickness. The single-blade system was used for this experiment.

The speed change (SC) mode for tape casting was developed based on our previous study [10]. The idea was to balance two of the following trends: continuous thickness decrease with processing time (as the hydraulic pressure behind the casting blade decreases), reduction of casting gap or increasing the carrier velocity, and the trend of thickness increase with enlargement of casting gap or slowing down the carrier movement. A change of casting gap during the casting process is not favourable as it demands the simultaneous screwing of two gap determining gauges on blade with micron-scale accuracy and, besides, needs the tape casting chamber to be open which can drastically affect the drying kinetics. Thus, it was chosen to compensate the decrease of tape thickness, associated with a pressure drop behind the casting blade, with tape thickening due to a decrease of carrier velocity. Taking into account mass conservation, the profile with which tape thickness reduces as the slurry filling in reservoir decreases was numerically calculated [10]. After testing the modelled program on LSM and LSM_CGO slurries in tape casting experiment, the program was corrected and exported to the process control machine (Figure 2).

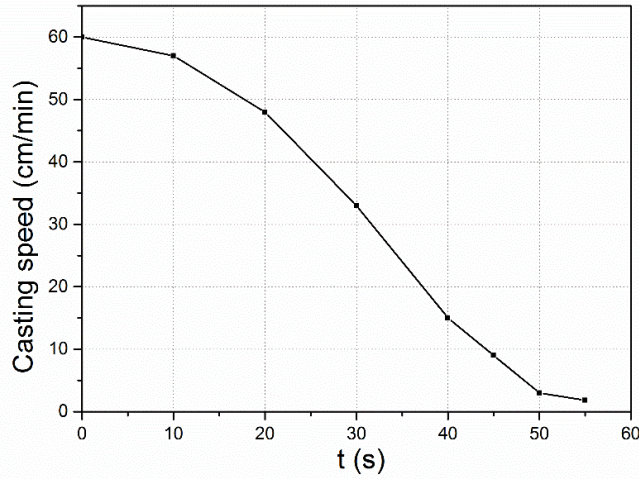


Figure 2. Casting program exported to the tape caster machine for steadying the dried tape thickness by continuous change of the casting speed.

3.2. Tape casting with varied length of the partition tongue.

All tests were carried out using the same LSM and LSM_CGO slurries with the same formulation and pre-casting rheological parameters as ones in the tape thickness control tests. The single blade tape casting unit has been applied. Experiments were conducted with different length of partition tongue at various casting speeds. Here, the partition tongue is the length of the Teflon partition beneath the casting blade, with a height identical to the casting gap of 1 mm, the width is equal to width of the whole partition, 1.95 mm; the maximum length of used partition matches the width of the casting blade of 6.5 mm and is referred to here as the whole (fraction of one) of the partition. The experiment sets were set as follows. First three experiments included co-casting of LSM and LSM_CGO slurries with the whole partition length and 10 cm/min, 15 cm/min and 30 cm/min casting speeds, consequently. Afterwards, the partition tongue was shortened by a quarter, the front edge was sharpened, and co-casting continued with a 0.75 fraction of partition with 20 cm/min and 30 cm/min alternately, *etc.* The shearing surface of blade was cleaned after each time and the sub-reservoirs were emptied in order to create reproducible conditions for each test.

4. Green tapes characterisation

The green tape thicknesses were measured both on LSM and LSM_CGO sides of the tape, about 2 cm from either edge of the tapes in order to neglect possible edge defects. Measurements were performed using a flat dual point digital micrometer of 15 mm in diameter at every 10 cm along the tape length. Precise collection of thickness data was necessary in order to track the general tendency of tape thickness regularities along the length.

Results and discussion

1. Tape casting in thickness control experiments

Figure 3 illustrates the thickness variation along the lengths of the LSM and LSM_CGO parts of the green tapes, produced by SB, DB and PS tape casting methods with 30 cm/min casting speed and by the SC casting mode. Similar tendencies in tape thickness consistency were detected for LSM and LSM_CGO slurries for all four tape casting modes.

Tapes are also shown to have a slightly different length because of a minor uncertainty in the initial slurry load in the reservoir. Since there was not an automatic control of slurry filling in the reservoir and slurry load was controlled manually, the difference in the resulting length of tapes was predictable and permissible. In order to ensure that thicknesses of tapes are compared when there was the same slurry level in tape caster, the curves correlated to tape thickness were aligned to the zero position, *i.e.* when the reservoir was empty in all casting modes.

Thickness irregularity at the start is pronounced when using the single blade for the tape casting (Figure 3) as the hydraulic pressure of the slurry column, accumulated behind the only casting blade, is ejected to the free space rapidly presumably resulting in a swelling effect. Swelling encounters when hydrostatic pressure pushes a large volume of slurry under the doctor blade so that the slurry exceeds the gap level. Swelling is normally determined by the height of the casting gap, polymer content in the slurry, slurry viscosity and casting speed. In other methods, the sharp release of a large amount of slurry onto the casting substrate was diminished due to either less slurry behind the casting blade like in the DB system or due to better control of hydrostatic pressure like in the cases of using SC and PS approaches.

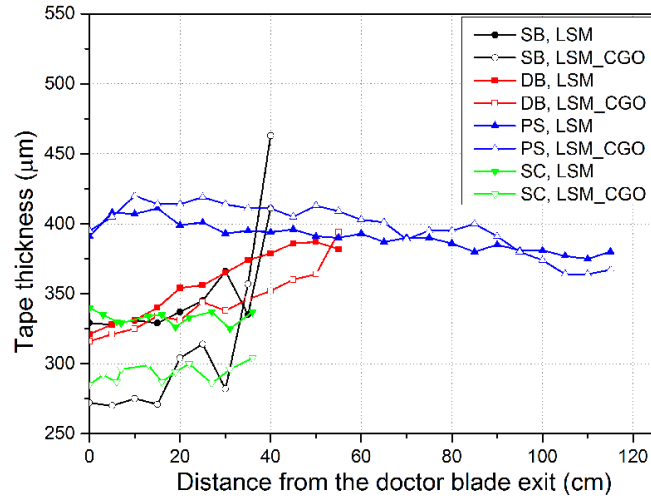


Figure 3. Thickness deviation of tapes, cast with usage of single-blade (SB), double-blade (DB), single blade and pump system (PS), single-blade and a program of casting speed change (SC). The estimated error in tape thickness measurement is 15 μm .

As for most other fluid forming techniques, the fluid flow for tape casting is determined by a complex combination of influencing factors, among which are the surface tension between slip and the moving carrier and, consequently, a side flow; air flow in the drying chamber affecting the drying kinetics; viscous friction of slurry and tape caster elements, shear thinning behaviour, etc. But the prevalent factor influencing the overall thickness variation in tape casting is the combination of the steady flow caused by the continuously moving carrier and irregular flow caused by the unfavourable decaying hydraulic pressure. A formula, which describes the influence of both shear- and pressure-driven forces on the thickness of a dried tape, was developed by Tok *et al.* [17] and considers the flow behaviour of non-Newtonian fluid using Ostwald-de Waele power law model (Eq. 1) (Table 1):

$$\delta_{tr} = \alpha\beta \frac{\rho_s}{\rho_{tr}} \left[\frac{1}{2} h_0 + \frac{2(h_0/2)^{\frac{1}{n}+2} (\Delta P)^{1/n}}{L(\frac{1}{n} + 2)k^{1/n}U} \right] \quad (2)$$

where δ_{tr} is a dried tape thickness, α the correction factor for side flow, β the correction factor for weight loss during drying, ρ_s the slurry density, ρ_{tr} the density of the formed tape, h_0 the casting gap, ΔP the hydraulic pressure exerted by the slurry column in a casting tank, L the length of the doctor blade in the casting direction, U the casting speed; k and n , as was described above, are slurry constants for the fluid consistency and the deviation from the Newtonian flow.

The simplest condition providing a uniform thickness across the entire tape length is when the actual slurry flow rate is equal to the carrier flow rate, *i.e.* the flow, determined just by the first term in Eq. 2, or when the actual slurry flow is constant for the whole duration of the casting process, *i.e.* when the flow rate, determined by the sum of both terms in Eq. 2 is constant during the whole casting process. The second concept is realized in the industrial tape casting by continuously pumping slurry into the tank maintaining a constant level of slurry in the tape caster reservoir, *e.g.* maintaining ΔP constant. The slight thickness changes of 7 and 9 % for LSM and LSM_CGO sides, respectively, were a result of adjusting casting and pumping speeds in the PS mode. Depending on the chosen slurry level which is analogue to the hydraulic pressure, the wet thickness might be even higher than the casting gap. In that case the slurry experiences the so-called swelling phenomena. An indirect method of measuring the swelling is comparing the thickness of tape obtained by a PS method and the stable part of a tape obtained by the SB method. For instance, for LSM slurry, cast with 30 cm/min speed and maintaining a slurry level in the reservoir of 22 mm, the swelling extent is found to be 70-80 μm (Figure 3). The direct method of measuring the swelling level is to measure the slurry trace on the side of the blade facing the drying area. The LSM slurry rise was 140-150 μm , which is higher than the values obtained from the analysis of the thickness curves in Figure 3.

An alternative method directed at minimizing the influence of the hydraulic pressure effect and maintaining the same level behind the casting blade is the DB approach. Tape thickness formed by DB tape casting was on average 10% smoother compared to the SB method. Nevertheless, the 20 % thickness gradient across the whole tape length was presumably because the gap under the rear blade was too high to keep the hydraulic pressure in the relief reservoir constant. As it is not the target of the current work, the choices of casting gaps were based on the study of Zhang *et al.* [16] and fixed at 1200 μm for the rear blade and 1000 μm for the front blade. Despite careful adjustment, the resulting tape thickness had a smoothly decaying character toward the end of the tape both in the LSM and LSM_CGO parts. At the end of the process, as expected, the tape thickness cast by DB mode was equal to the thicknesses of tapes, cast with the SB and SC methods. Further optimisation on the adjustment of the gaps in the double blade set-up was discontinued due to the presence of a vortex flow in the relief reservoir, proven both experimentally [18] and numerically [19]. The vortex flow affecting the rheological behaviour of the slurry makes a shearing flow during casting uncontrollable. Together with a complicated design of partition required to separate both reservoirs and both gaps under the blades, the DB approach was shown to be not applicable for the control of the multiple material flow applied in the current SBS TC work.

In the newly implemented technique SC, tape thickness was prescribed by a change in the casting speed U due to the decrease of the slurry pressure head ΔP . As a result, thickness irregularities stayed within 5%, identifying the SC approach as a well-controlled tool. The thickness values achieved on both the LSM and LSM_CGO sides of the graded tape are in good correspondence to the thickness values of the tape, produced by SB tape casting, exactly as the speed change program was settled and optimized. Despite the fact that the SC approach forms the smoothest dried tapes, this method should be applied with care, as the continuous

change of casting speed can lead to a change of microstructure and, consequently, porosity if the elongated particles and/or pore formers are in use. Moreover, the chosen pseudoplastic slurries have to have a plateau in the viscosity curves at the applied casting shear rates. Otherwise, slurry is not stable during the tape casting, which usually leads to morphological irregularities in green and sintered tapes.

Based on the conducted study, the novel casting speed change mode and tape casting using a pump system was shown to form smooth tape surfaces. The use of pump system in tape casting, however, is highly recommended if a large slurry volume is to be cast so that the high losses caused by the time, required to adjust casting and pumping speed during slurry supply, are reasonable. The use of the SC program was also eliminated for further SBS TC test, as the shear rate profile, determining the quality of the interface [11], was proven to be dependent on the casting speed [20]. For the same reasons of high possibility of unstable flow [19] during co-casting, the work with a DB set-up was discontinued. Considering the detailed study of the multiple materials co-flow in a lab-scale tape casting, the SB approach was decided to be applied for further SBS TC tests.

2. Tape casting with varied length of the partition tongue

The partition width of about 2 mm was chosen as it was complicated to set a thinner partition precisely in the middle of the tank. Besides, it is also challenging to fasten a thinner partition tight to the tank walls, causing leaking of slurries in between adjacent reservoirs at the seams. The use of thick partitions would hinder the merging of co-flowing slurries and would limit the use of highly viscous slurries with confined side flow.

During the primary experiments on SBS TC it was found that a tapered front edge of the partition was required since a blunt flat partition was shown to leave traces on the dried green tape and lead to undesired inhomogeneity at the interface area (Figure 4). These traces on the tape surface were a consequence of the significant distance, which was created by the blunt partition and which co-casting viscous slurries had to overflow just by flowing aside. Typical for highly viscous slurries limited side flow and rapid evaporation of organic solvent happening right after the doctor blade region hindered merging of two adjacent slurries and impeded a complete healing of the co-flowing gap. The two solutions were found to overcome this challenge. The first solution included the use of less viscous slurries, which was shown to affect the shape of the interface and final thickness [11]. Another solution was sharpening the partition at the front edge in order to create a smooth merging for co-casting slurries and thinning the confluence area (Figure 4). The use of the sharpened partition opened a chance to co-cast slurries with a wide variety of viscosity values including highly viscous ones.

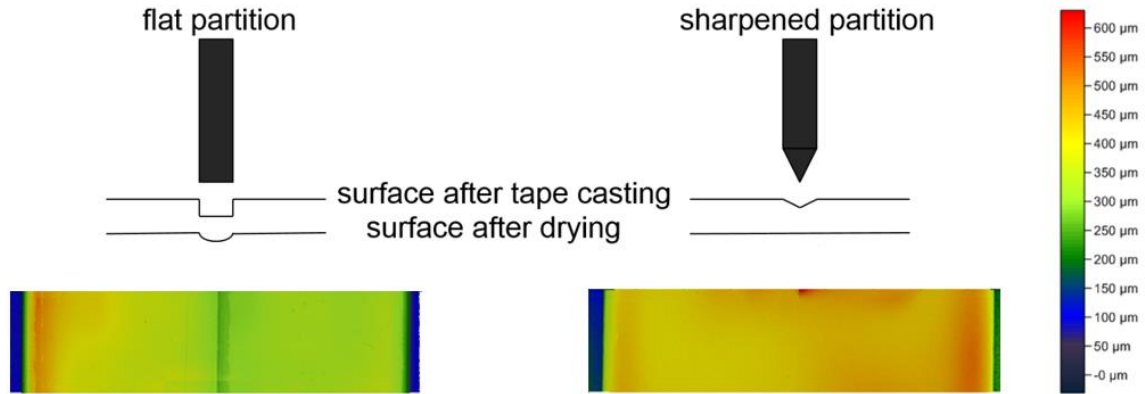


Figure 4. Schematic representation of surfaces of green graded tapes after co-casting using a non-sharpened and sharpened partition and below the pictures of surface topography of green tape samples, which were analysed by means of laser profilometry. The short slit on the sample, cast with the tapered partition, was made by knife in order to later identify the interface region on a completely smooth graded tape. The length of each piece of tape was 20 mm, and the width was 80 mm.

To examine the effects of partition design and casting speed on slurry flow behaviour, a number of experiments were carried out. Each dot in Figure 5a corresponds to a SBS TC experiment, carried out at casting speeds in a range from 10 cm/min to 50 cm/min, and various lengths of the partition tongue (Figure 5b). The dots marked in grey colour (Figure 5a) represent experiments, where the co-cast slurries did not merge and a gap in interface area was formed (inlet in Figure 5a). The ability of adjacently cast slurries to merge in the confluence area and form an interface was shown in general to grow as the casting speed was reduced and the partition tongue shortened.

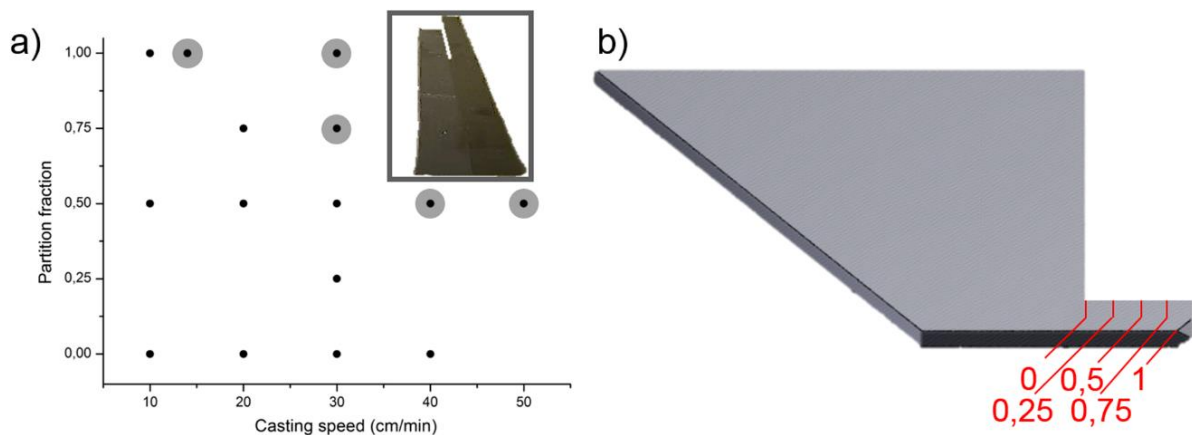


Figure 5. a) Experiments identifying the effect of the partition design and casting velocity; grey dots denote co-casting experiments where the splitting between co-cast materials was observed (an example is shown in the inset); b) Side view of a Teflon partition wall; red lines show the way of cutting the partition length.. The numbers indicate the fraction of partition tongue which was used in the experiment.

The ability of adjacently cast slurries to merge in the confluence area and form an interface was shown to grow as the casting speed was reduced and the partition tongue was shortened (Figure 5a). To indicate the influence of flow behaviour on the formation of the graded tape, the tape casting process was reproduced on a rheometer according to shear rates applied to slurries during each step of the real casting process. Basically, tape casting is a shearing processes (Figure 6): first, we pour slurries into a reservoir applying a certain shear rate about 5 s^{-1} , later we keep slurries in the reservoir for 10-15 s in order to remove any effects of the rheological history of the slurries. Afterwards, the casting process starts where shear rates can be approximately evaluated as the casting speed divided by the size of the gap under the blade; and the last step is drying, which we here assume as a step where no shear stresses are applied, ignoring the shrinkage stress and possible edge effects. However, in order to be able to measure the viscosity, a minor shear rate of 0.1 s^{-1} was applied on that last step of the rheological program. During this multistep program the, viscosity of LSM and LSM_CGO slurries were measured as a response to the applied shear rates. For SBS TC of an adjacently graded tape with a steep interface it is required [11] for the LSM and LSM_CGO viscosity curves to have a similar rheological response at each of described steps.

Figure 6a illustrates changes in LSM and LSM_CGO rheological behaviour during the test imitating tape casting at 10 cm/min casting speed. Tracking the flow field in the tape caster unit, three clear regions of characteristic viscosity changes are identified: (i) after pouring slurries into the tape caster reservoir and allowing the slurry to rest, the molecules of binder in the highly viscous slurries start to form a polymeric matrix increasing the viscosity of the slurries; (ii) under an applied shear rate polymeric chains elongate causing the uniform viscous flow of slurries under the casting blade; (iii) when slurries flow in a free space, reciprocal action of the polymeric matrix formation and the drying process increases the viscosities of the slurries. Hence, the changes in the system are caused by both shear thinning behaviour of casting slurries and the drying process.

The thixotropic behaviour, characteristic for both LSM and LSM_CGO_4 slurries, requires approximately 7 s to 10 s to completely recover the initial structure and retrieve initial viscosity. During that time the slurry is assumed to be a fluidly deformable. The fluidly deformable state is a state of cast tapes at the initial stage of the drying process when the dried film is still not formed at the tape surface and its edges are capable of shifting under the weight of the tape.

Low viscosity, typical for slurries passing the blade region, allows the slurry to flow aside under the influence of gravity, surface tension forces and levelling without revealing stresses in surfaces. Thus, complete absence or a short partition tongue below the blade favours the merging of the co-flowing slurries and formation of a uniform interface. When the partition tongue divides the co-flowing slurries all the way under the blade, the slurries are free to flow aside just after passing the blade region. Casting with a speed of 10 cm/min, the fluidly deformable state of slurries lasts for at least 7 s to 10 s. That time was proven (Figure 6a) to be enough for slurries to merge and form an interface.

However, when the slurries are cast faster, the duration when slurries are fluidly deformable drastically shortens (Figure 6b). Thus, the faster the casting speed, the lower is the possibility for co-casting slurries to merge when the whole partition tongue is used (horizontal tendency in Figure 5a). For instance, in the current work the small change in casting speed from 10 cm/min to 14 cm/min results in splitting between co-cast materials (Figure 5a).

Another noteworthy result is the shortening of the shearing time with an increase of the casting speed. For example, when the partition tongue divides the casting gap at a fraction of 0.75 of the blade width, the time, during which slurry has a low viscosity at the casting speed of 10 cm/min is 6 s (Figure 6a) and less than 3 s for a casting speed of 30 cm/min (Figure 6b). Thus, the time for adjacent flowing slurries to merge in the partition free area beneath the blade is 1.5 s and less than 0.75 s for 10 cm/min and 30 cm/min casting speeds, respectively. The results show (Figure 5a) that 1.5 s in a low viscosity state is enough for adjacent slurries to join in the confluence area of 1.95 mm (the width of the partition), while 0.75 s is too short time for slurries to flow aside and form the interface.

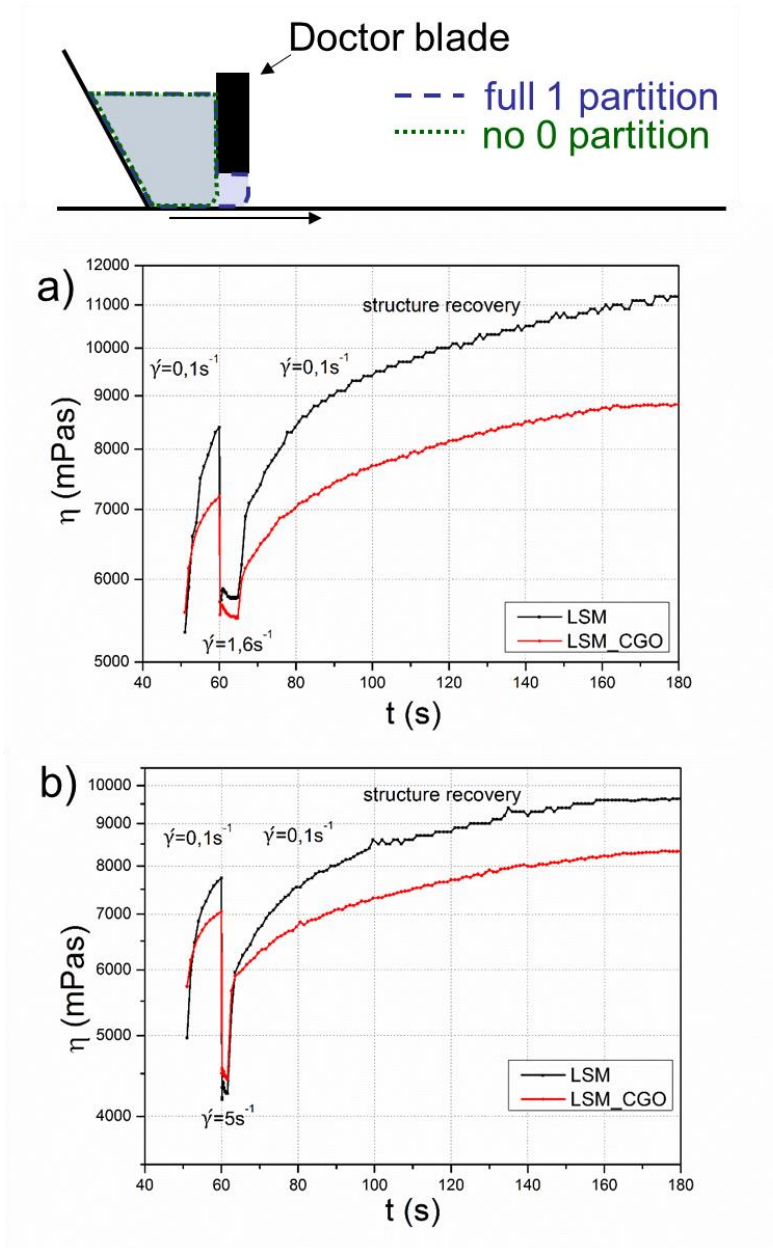


Figure 6. Structure recover test for LSM and LSM_CGO slurries co-cast at a) 10 cm/min and b) 30 cm/min casting speed.

Normally, gravity is ignored in tape thickness studies as it is assumed that its effect is negligible for tape dimensional consistency, but in SBS TC an accurate determination and tuning of all parameters, which influence the forming of the confluence interface area, is of

great importance. The study of the impact of gravity was built on the well-known fact that the tape thickness decreases when the casting speed is increased [11]. Thus, the tape thickness of the same slurry was shown to be halved when the casting velocity was increased from 10 cm/min to 40 cm/min [11]. In order to estimate the role of gravity forces on the side flow effect (the correction factor for side flow α in Eq.2), three 80 mm wide tapes were cast manually on a laser profilometer substrate covered with a Mylar film. The speed was about 80 cm/min and casting gaps of 1000 μm , 500 μm , and 90 μm were chosen. LSM slurry was used for all three experiments. The laser profilometer was used in order to measure the tape thickness gradient in-situ. Results showed (Figure 7) that the side flow of tapes cast with a 1000 μm gap, which was supposed to represent tape casting with slow casting speeds, exceeded 10 mm ($\alpha=0.89$), while for the tape cast with 500 μm ($\alpha=0.96$) and 90 μm ($\alpha=1$) gaps, which were supposed to refer to faster casting, these numbers were 3.5 and 0 mm, consequently. In the experiment with a casting speed change, proportional change in tape thicknesses would lead to the proportional changes in side flow. When the partition creates a 1.95 mm wide confluence area to be filled by co-cast slurries from both sides, the side flow plays a crucial role. However the side flow is of practical value as long as slurries are able to flow, i.e. being at low viscous state.

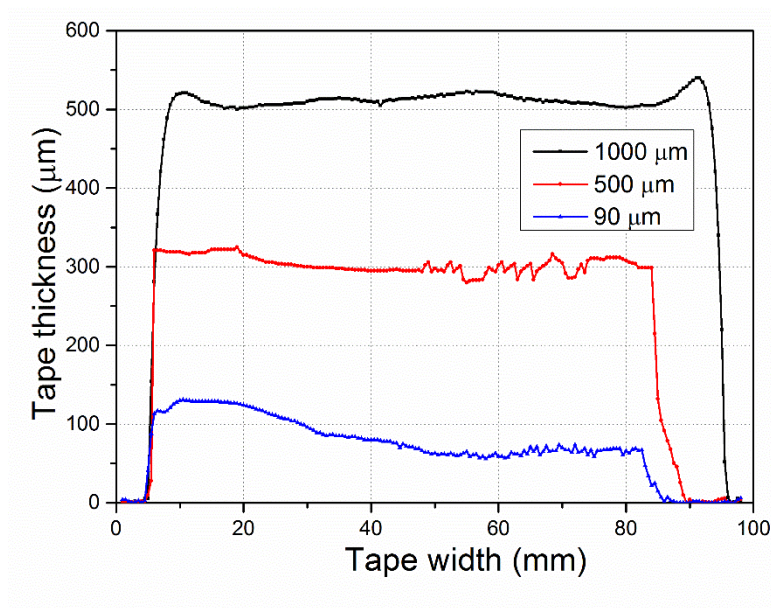


Figure 7. Cross-section profile of the LSM slurries made on a laser profilometer showing the side flow effect.

Conclusion

Tape casting with a single blade, double blade, with use of a pump system and tape casting with a continuous speed change have been compared in order to cast tapes with a uniform tape thickness. The proposed method of consistent casting speed change showed the minimum of tape thickness gradient of 5% along the casting length. However, this method requires the use of stable slurries with particles as close as possible to a spherical morphology (with no elongations). The use of a pump system in order to maintain the same slurry level in the casting reservoir exhibited about 10% of thickness gradient. A better representation of this test would presumably be possible if a larger amount of slurry was cast because of the required adjustment of casting and pumping speeds. The use of double blade to support the

same level behind the casting reservoir also showed an unexpected thickness fluctuation. Better results might be achieved if the casting gaps below both blades were adjusted. This work has been discontinued because of the presence of the vortex when high viscous slurries are applied [19]. Single blade was chosen for SBS TC process in the small lab-scale as it shows relatively small thickness gradient of below 10% after the cast first 10 mm. Moreover, the use of the single blade guarantees a stable flow with well-studied pressure and shear impacts on the tape formation.

The influence of partition geometry on the quality of the graded tape was also presented. It was shown that the chance to obtain a uniform adjacently graded tape decreases with an increase of the length of the partition tongue beneath the casting blade and with an increase in casting speed. Moreover, unlike the regular practice in shaping techniques, where rheological study of processing slurries and their numerical description are limited by providing viscosity and flow curves, a new approach of describing and measuring slurries fluid behaviour was proposed. The distinctive difference between the proposed approach and a routine rheological examination of pre-casting slurry is consideration of rheological test as the representation of dynamic sequence of tape casting process. Nevertheless, the application of a standard rheological program with pre-shear and increasing shear rate is required in order to analyse and be able to compare shear thinning behaviour of casting slurries.

References

- [1] G. N. Howatt, "Method of producing high dielectric high insulation ceramic plates," US2582993 A, 22-Jan-1952.
- [2] H. Loest, R. Lipp, and E. Mitsoulis, "Numerical flow simulation of viscoplastic slurries and design criteria for a tape casting unit," *J. Am. Ceram. Soc.*, vol. 77, no. 1, pp. 254 – 262, 1994.
- [3] A. R. Dinesen, S. Linderorth, N. Pryds, and A. Smith, "A magnetic regenerator, a method of making a magnetic regenerator, a method of making an active magnetic refrigerator and an active magnetic refrigerator," PCT/EP2005/013654, 20-Jul-2006.
- [4] "Method for manufacture of transparent ceramics." 21-Sep-2010.
- [5] E. R. Kupp, G. L. Messing, J. M. Anderson, V. Gopalan, J. Q. Dumm, C. Kraisinger, N. Ter-Gabrielyan, L. D. Merkle, M. Dubinskii, V. K. Simonaitis-Castillo, and G. J. Quarles, "Co-casting and optical characteristics of transparent segmented composite Er:YAG laser ceramics," *J. Mater. Res.*, vol. 25, no. 03, pp. 476–483, Jan. 2011.
- [6] H. Yang, P. Zhang, Q. Wu, H. Ge, and M. Pan, "Effect of monovalent metal substitution on the magnetocaloric effect of perovskite manganites $\text{Pr}_{0.5}\text{Sr}_{0.3}\text{Mn}_{0.2}\text{MnO}_3$ (M=Na, Li, K and Ag)," *J. Magn. Magn. Mater.*, vol. 324, no. 22, pp. 3727–3730, Nov. 2012.
- [7] M. Wu and G. L. Messing, "Fabrication of Oriented SiC-Whisker-Reinforced Mullite Matrix Composites by Tape Casting," *J. Am. Ceram. Soc.*, vol. 77, no. 10, pp. 2586–2592, Oct. 1994.

- [8] D.-S. Park and C.-W. Kim, "A modification of tape casting for aligning the whiskers," *J. Mater. Sci.*, vol. 34, no. 23, pp. 5827–5832, Dec. 1999.
- [9] R. E. Mistler and E. R. Twiname, *Tape Casting: Theory and Practice*. Wiley-American Ceramic Society, 2000, p. 298.
- [10] M. Jabbari, R. Bulatova, J. H. Hattel, and C. R. H. Bahl, "Quasi-steady state power law model for flow of $(\text{La}_{0.85}\text{Sr}_{0.15})_{0.9}\text{MnO}_3$ ceramic slurry in tape casting," *Mater. Sci. Technol.*, vol. 29, no. 9, pp. 1080–1087, Sep. 2013.
- [11] R. Bulatova, M. Jabbari, A. Kaiser, M. Della Negra, K. B. Andersen, J. Gurauskis, and C. R. H. Bahl, "Thickness control and interface quality as functions of slurry formulation and casting speed in side-by-side tape casting," *J. Eur. Ceram. Soc.*, Jul. 2014.
- [12] *Solid Oxide Fuel Cells VIII: (SOFC VIII) : Proceedings of the International Symposium, Volume 8*. The Electrochemical Society, 2003, p. 1520.
- [13] *Inorganic Membranes: Synthesis, Characterization and Applications: Synthesis, Characterization and Applications (Google eBook)*. Elsevier, 2008, p. 480.
- [14] H. Raeder, C. Simon, T. Chartier, and H. L. Toftegaard, "Tape casting of zirconia for ion conducting membranes: A study of dispersants," *J. Eur. Ceram. Soc.*, vol. 13, no. 6, pp. 485–491, Jan. 1994.
- [15] R. Bulatova, C. Bahl, K. Andersen, L. T. Kuhn, and N. Pryds, "Functionally Graded Ceramics Fabricated with Side-by-Side Tape Casting for Use in Magnetic Refrigeration," *Int. J. Appl. Ceram. Technol.*, p. n/a–n/a, Aug. 2014.
- [16] G. Zhang, Y. Wang, and J. Ma, "Bingham plastic fluid flow model for ceramic tape casting," *Mater. Sci. Eng. A*, vol. 337, no. 1–2, pp. 274–280, Nov. 2002.
- [17] A. I. Y. Tok, F. Y. C. Boey, and Y. C. Lam, "Non-Newtonian fluid flow model for ceramic tape casting," *Mater. Sci. Eng. A*, vol. 280, no. 2, pp. 282–288, Mar. 2000.
- [18] M. Schmidt, H. Münstedt, M. Svec, A. Roosen, T. Betz, and F. Koppe, "Local Flow Behavior of Ceramic Slurries in Tape Casting, as Investigated by Laser-Doppler Velocimetry," *J. Am. Ceram. Soc.*, vol. 85, no. 2, pp. 314–320, Dec. 2004.
- [19] A. Wonisch, P. Polfer, T. Kraft, A. Dellert, A. Heunisch, and A. Roosen, "A Comprehensive Simulation Scheme for Tape Casting: From Flow Behavior to Anisotropy Development," *J. Am. Ceram. Soc.*, vol. 94, no. 7, pp. 2053–2060, Jul. 2011.
- [20] M. Svec, M. Schmidt, T. Betz, A. Roosen, F. Koppe, and H. Münstedt, "The influence of different blade geometries on the local flow behavior of ceramic slurries in the tape casting unit," *Ceram. Forum Int.*, vol. 79, no. 5, pp. E39–E43, 2002.